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The crystal structures of $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$

By NOBUKAZU NIIZEKI and MASATADA WACHI*

The Electrical Communication Laboratory, Nippon
Telegraph and Telephone Public Corporation, Musasino-si, Tokyo

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Auszug

Aus Schmelzen von der Zusammensetzung $Bi_2O_3 \cdot 2M_2O_3$, M = Mn, Al, Fe, mit einem Überschuß von Bi_2O_3 als Flußmittel wurden Kristalle von $Bi_2Al_4O_9$, $Bi_2Fe_4O_9$ und $Bi_2Mn_4O_{10}$ gewonnen; ihre Strukturen wurden bestimmt. Alle Kristalle gehören zur Raumgruppe *Pbam*. Die Gitterkonstanten sind für

$Bi_2Al_4O_9$: $a = 7{,}712$ Å, $b = 8{,}112$ Å, $c = 5{,}708$ Å
$Bi_2Fe_4O_9$: $a = 7{,}905$ Å, $b = 8{,}428$ Å, $c = 6{,}005$ Å
$Bi_2Mn_4O_{10}$: $a = 7{,}540$ Å, $b = 8{,}534$ Å, $c = 5{,}766$ Å.

Die Elementarzelle enthält zwei Formeleinheiten. Die Struktur wurde durch Deutung von Patterson-Schnitten für $z = 0$, $\frac{1}{2}$ und $\frac{1}{4}$ bestimmt und aus dreidimensionalen Intensitätsdaten nach der Ausgleichsmethode verfeinert bis zu R-Werten von 0,11, 0,12 und 0,10 für die Mn-, Al- bzw. Fe-Verbindung.

$Bi_2Al_4O_9$ und $Bi_2Fe_4O_9$ haben die gleiche Struktur. Al und Fe werden vom Sauerstoff zum Teil oktaedrisch, zum anderen tetraedrisch umgeben. In den Kristallen von $Bi_2Mn_4O_{10}$ ist die oktaedrische Umgebung durch eine tetragonalpyramidale ersetzt. Bi hat drei nächste Sauerstoff-Nachbarn mit fast senkrecht auf einanderstehenden (Bi—O)-Richtungen und außerdem fünf entferntere.

Abstract

The crystal structures of $Bi_2Mn_4O_{10}$ ($BiMn_2O_5$), $Bi_2Al_4O_9$, and $Bi_2Fe_4O_9$ have been analyzed. Single crystals of these compounds were grown from the melt of the composition $Bi_2O_3 \cdot 2M_2O_3$ (M = Mn,Al,Fe) with excess Bi_2O_3 added as a flux. These crystals are all orthorhombic, and their unit-cell dimensions are:

$Bi_2Mn_4O_{10}$: $a = 7.540$ Å, $b = 8.534$ Å, $c = 5.766$ Å
$Bi_2Al_4O_9$: $a = 7.712$ Å, $b = 8.112$ Å, $c = 5.708$ Å
$Bi_2Fe_4O_9$: $a = 7.905$ Å, $b = 8.428$ Å, $c = 6.005$ Å.

* Present address: Department of Chemistry ,Tokyo University, Bunkyo-ku, Tokyo, Japan.

These unit cells contain two formula units. Space groups are all *Pbam*. Three-dimensional intensity data was collected by multiple-film integrating Weissenberg photography. The structures were analyzed by interpretation of Patterson sections at $z = 0$, $\frac{1}{2}$, and $\frac{1}{4}$, and refined by the least-squares method. The absorption and dispersion corrections were included in data processing. The final R value are 0.11, 0.12, and 0.10 for Mn, Al, and Fe compound respectively.

Two compounds $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$ are isostructural. One kind of Al(Fe) is octahedrally coordinated by six oxygen atoms, and the other kind tetrahedrally by four oxygen atoms. The structure of the Mn compound differs from the other two only in that one oxygen atom located at $00\frac{1}{2}$ in the others is replaced by two oxygen atoms at 0,0, $\pm$ 0.281, and as the result, Mn(2) is coordinated by five oxygen atoms in a square-pyramidal configuration. The coordination of oxygen atoms around Bi is similar to that of sulfur in sulfosalts containing Bi; there are three short Bi—O bonds mutually orthogonal, and five more longer bonds.

Introduction

In the course of systematic studies on the ceramic specimens of the oxide systems Bi_2O_3—Mn_2O_3, Bi_2O_3—Al_2O_3, and Bi_2O_3—Fe_2O_3, three new compounds were found. These compounds were identified by the x-ray powder-diffraction patterns of the ceramics obtained by firing the starting materials mixed in the composition $Bi_2O_3 \cdot 2M_2O_3$, where M stands for Mn, Al, and Fe. Preliminary study on the system Bi_2O_3—Fe_2O_3 was reported by KOIZUMI, NIIZEKI, and IKEDA[1]. These compounds were briefly described by LEVIN and ROTH[2] as $Bi_2O_3 \cdot 2Mn_2O_3$, $Bi_2O_3 \cdot 2Al_2O_3$, and $Bi_2O_3 \cdot 2Fe_2O_3$. A short account of the structure analysis of these compounds was reported by TUTOV *et al.*[3], in which the Mn compound was identified as $Bi_2O_3 \cdot 2Mn_2O_{3.4}$. Complete description of these structures has not been presented.

Preliminary crystallographic studies

Powder-diffraction patterns of the three compounds obtained with Cu$K\alpha$ radiation are schematically shown in Fig. 1. These patterns could be indexed on the basis of the orthorhombic unit cells, dimen-

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[1] H. KOIZUMI, N. NIIZEKI and T. IKEDA, An x-ray study on Bi_2O_3—Fe_2O_3 system. Jap. J. Appl. Physics **3** (1964) 495—496.

[2] E. M. LEVIN and R. S. ROTH, Polymorphism of bismuth sesquioxide. II. Effect of oxide addittions on the polymorphism of Bi_2O_3. J. Res. NBS **68**A (1964) 197—206.

[3] A. G. TUTOV, I. E. MYL'NIKOVA, N. N. PARFENOVA, V. A. BOKOV and S. A. KIZHAEV, New compounds in the system Bi_2O_3—Me_2O_3(Fe^{+3}, Al^{+3}, Ga^{+3}, Mn^{+3}). Soviet Physics—Solid States **6** (1964) 963—964.

sions of which are listed in Table 1, and the assigned indices are indicated in Fig. 1. Similarities in the diffraction patterns of $Bi_2O_3 \cdot 2Al_2O_3$, and $Bi_2O_3 \cdot 2Fe_2O_3$ are clearly observed, and can be explained if these two are isostructural since the unit cell of the latter is uniformly larger than that of the former due to the larger ionic size of Fe^{+3} than Al^{+3}. Dissimilarity of the pattern of Mn compound to the other two is also apparent in Fig. 1, and the difference

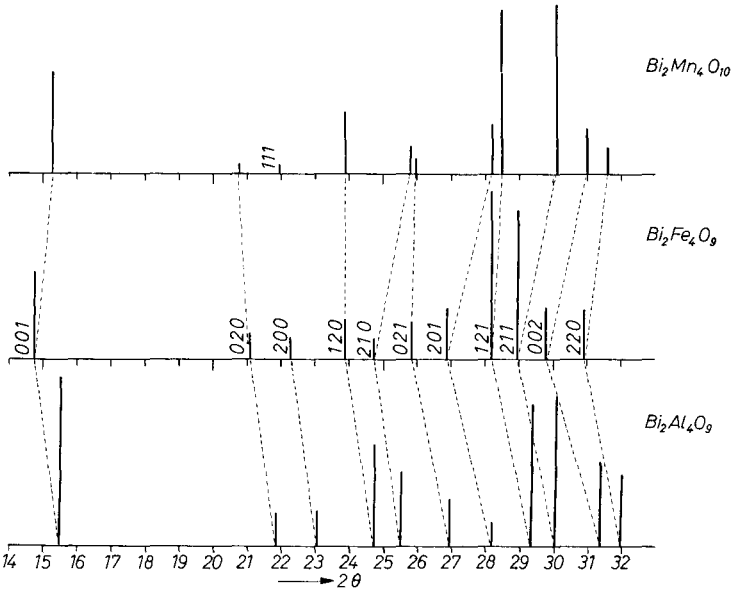


Fig. 1. Graphical representation of x-ray powder-diffraction patterns of $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$, and $Bi_2Fe_4O_9$. Patterns were obtained by diffractometer with Cu$K\alpha$ radiation

suggests that the structural scheme of the compounds is somewhat different from that of the Al and Fe compound. The unit cell of the Mn compound is found to be similar to that of $HoMn_2O_5$ described by QUEZEL-AMBRUNAZ *et al.*[4]. The reported lattice constants of the last compound are $a = 7.36$, $b = 8.49$, and $c = 5.69$ Å.

Single crystals of the three compounds were all grown by the flux method. Mixture of oxides, $Bi_2O_3 + 2M_2O_3$, were melted with excess amount of Bi_2O_3 in Pt crucible at the temperature above

[4] S. QUEZEL-AMBRUNAZ, F. BERTAUT and G. BUISSON, Structure des composés d'oxyde de terres rares et de manganèse de formule TMn_2O_5. Compt. rend. Acad. Sci. [Paris] **258** (1964) 3025–3027.

Table 1. *Crystallographic properties of* $Bi_2Mn_4O_{10}$ $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$

	$Bi_2Mn_4O_{10}$	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$
Color	black	colorless	light tan
Luster	submetallic	transparent	transparent
Habit	prismatic (octagonal)	thin tabular to square prism	thin tabular to square prism
Forms	{100} {010} {110} {1$\bar{1}$0} {001}	{110} {1$\bar{1}$0} {001}	{110} {1$\bar{1}$0} {001}
Lattice constants a	7.540 Å ± 0.005 Å	7.712 Å ± 0.005 Å	7.950 Å ± 0.005 Å
b	8.534	8.112	8.428
c	5.766	5.708	6.005
Space group	$D_{2h}^{19} \sim Pbam$	$Pbam$	$Pbam$
Cell content	2	2	2
Sample dimension, R	0.0008 cm	0.0020 cm	0.0016 cm
Absorption factors			
μ	1474 cm^{-1}	987 cm^{-1}	1406 cm^{-1}
μR	1.18	1.97	2.25
Density			
measured	7.133 ± 0.005		
calculated	6.979 ($Bi_2Mn_4O_9$)	7.121 ($Bi_2Mn_4O_{10}$)	

900 °C for 12 hours. Cooling of the melt was carried out at a rate of about 7 °C per hour to 800 °C, and the power to the furnace was turned off. The synthesized crystals were extracted from the solidified mass by immersing the entire crucible in a hot nitric acid. Dimensions of the obtained crystals were up to 0.5 × 0.3 × 0.3 mm. The color, luster, habit, and crystal forms of the three kinds of crystal are summarized in Table 1.

Lattice constants and space group of the three compounds are also listed in Table 1. The lattice constants were determined from precession and Weissenberg photographs, and space group from the observed systematic extinctions; $h0l$ reflections with h odd, and $0kl$ reflections with k odd are missing. These unit cells contain two formula units. A test for piezoelectricity gave a negative result and thus a centrosymmetric group *Pbam* was uniquely assigned.

To determine the number of oxygen atoms in the chemical formula of Mn compound, density measurement with a pycnometer was carried out on the single crystals. The measured value was compared with calculated values assuming two formulae, $Bi_2Mn_4O_9$ ($Bi_2O_3 \cdot 2Mn_2O_3$) and $Bi_2Mn_4O_{10}$ ($BiMn_2O_5$), as shown in Table 1. A good agreement with the latter established the correct formula of the compound. It is to be noted that if the compound is a stoichiometric one, two kinds of valency, i.e. trivalent and tetravalent valencies have to be assigned to manganese ions. The correct formula is to be expressed as $Bi_2Mn_2^{+3}Mn_2^{+4}O_{10}$.

Structure analysis

Intensity data of all the three kinds of crystal were collected by equi-inclination integrating Weissenberg camera with multiple-film technique, and c-axis photographs were taken with Cu$K\alpha$ radiation up to the third level for Mn and Al compound, and the second level for Fe compound. Intensities were measured by visual comparison with a standard intensity scale. Absorption corrections were performed assuming cylindrical shapes with radii obtained by averaging the lengths in the square cross sections of the prismatic crystals. The radii of cylinders and the absorption factors of the crystals used in the experiments are summarized in Table 1. For the correction of the higher-level reflections BUERGER and NIIZEKI's method[5] was used. Intensities were then corrected for the usual Lorentz and polarization factors, and $F^2_{obs}(hkl)$ values were placed on an absolute basis by WILSON's method.

The structure analyses of the three crystals were all carried out by the following procedure.

Since the lengths of c axes are about 6 Å, and there exist mirror planes parallel to (001) at $z = 0$ and 1/2 in space group $Pbam$, it was deduced that all atoms in the unit cell are to be located at $z = 0$, 1/2, or nearly 1/4. Thus the three-dimensional Patterson sections at the above z values were synthesized. The atomic coordinates of Bi and other lighter metals were easily determined from the sections. Locations of oxygen atoms were successively made clear after a few trials of $(F_{obs} - F_{metal})$ difference Fourier syntheses.

It was confirmed at this stage that the structures of $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$ are essentially identical, and that the structure of $Bi_2Mn_4O_9$

[5] M. J. BUERGER and N. NIIZEKI, Correction for absorption for rod shaped single crystal. Amer. Mineral. **43** (1958) 726–728.

differs from the above two in one aspect. In the former two structures, one oxygen atom was found at $x = 0$, $y = 0$, $z = 1/2$, i.e. at equipoint $2b$ of *Pbam*, while in the latter structure oxygen atoms at the same x and y coordinates were found in sections at $z = 1/4$ and $3/4$, i.e. at

Table 2. *Final atomic parameters of* $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$ *and* $Bi_2Fe_4O_9$

		$Bi_2Mn_4O_{10}$	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$
Bi	x	0.1597 ± 0.0003	0.1704 ± 0.0004	0.1761 ± 0.0006
	y	0.1643 0.0003	0.1668 0.0003	0.1715 0.0005
	z	0	0	0
	B	0.58 0.04	0.49 0.05	1.12 0.08
M(1)*	x	1/2	1/2	1/2
	y	0	0	0
	z	0.262 ± 0.003	0.257 ± 0.005	0.257 ± 0.008
	B	0.58 0.1	0.7 0.4	1.15 0.37
M(2)	x	0.407 ± 0.001	0.347 ± 0.003	0.351 ± 0.002
	y	0.354 0.001	0.339 0.003	0.334 0.002
	z	1/2	1/2	1/2
	B	0.65 0.1	0.8 0.4	1.25 0.32
O(1)	x	0	0	0
	y	0	0	0
	z	0.281 ± 0.01	1/2	1/2
	B	0.8	1.0	1.5
O(2)	x	0.386 ± 0.004	0.380 ± 0.006	0.373 ± 0.007
	y	0.176 0.004	0.201 0.005	0.198 0.006
	z	0.250 0.008	0.251 0.007	0.243 0.014
	B	0.6	1.1	1.0
O(3)	x	0.147 ± 0.006	0.140 ± 0.007	0.137 ± 0.010
	y	0.418 0.005	0.433 0.007	0.418 0.010
	z	1/2	1/2	1/2
	B	0.6	1.0	1.2
O(4)	x	0.147 ± 0.006	0.143 ± 0.008	0.143 ± 0.010
	y	0.425 0.005	0.426 0.007	0.415 0.010
	z	0	0	0
	B	0.6	1.1	1.6
R**		0.11	0.12	0.10

* M Mn, Al or Fe.

** R Reliability factor defined as $\dfrac{\Sigma\,||F_{obs}| - |F_{calc}||}{\Sigma\,|F_{obs}|}$

equipoint $4e$. Since the number and coordinates of the other oxygen atoms were same for the two types of the structure, it was proved that the number of oxygen atoms in the formula is 9 for the Al and Fe compounds, and 10 for Mn compound.

The obtained structures were then refined by the three-dimensional least-squares method. At this stage the effect due to the anomalous dispersion was corrected. Three to five cycles of refinement with diagonal approximation and without a special weighting system were performed by the computer NEAC 2206 of the laboratory. The numbers of reflections used in the refinements are 308, 266 and 248 for Mn, Al, and Fe compound respectively.

The final atomic coordinates and temperature factors are tabulated in Table 2 for the three crystals. The final values of R are 0.11, 0.12

Table 3. *Observed and calculated structure factors of* $Bi_2Mn_4O_{10}$

h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c
2 0 0	10	17	4 7 0	105	105	2 5 1	203	216	1 3 2	146	-155	5 1 3	42	49
4	183	-174	5	41	- 41	3	84	- 85	2	5	- 6	6	42	46
6	185	199	6	21	14	4	94	- 93	3	295	280	7	53	63
8	28	36	7	21	27	5	23	19	4	30	34	8	86	- 86
1 1 0	10	19	0 8 0	39	- 30	6	53	- 47	5	39	39	0 2 3	60	- 69
2	115	-134	1	92	-116	7	46	43	6	5	2	1	176	-195
3	141	-144	2	83	81	8	77	82	7	89	- 68	2	81	68
4	196	203	3	21	8	0 6 1	149	156	8	22	- 29	3	85	- 73
5	29	- 30	4	104	89	1	30	33	0 4 2	311	-259	4	74	63
6	5	16	5	131	132	2	107	- 99	1	174	140	5	125	136
7	22	6	6	47	- 29	3	32	33	2	43	- 37	6	64	- 70
8	165	-162	1 9 0	134	-109	4	97	- 93	3	21	- 17	7	53	- 60
9	78	- 75	2	19	13	5	10	- 7	4	41	43	8	14	20
0 2 0	56	- 56	3	111	107	6	192	158	5	127	-151	1 3 3	81	- 75
1	131	-154	4	15	22	7	15	- 10	6	83	-101	2	19	- 25
2	124	135	5	42	- 54	1 7 1	23	20	7	119	109	3	162	181
3	23	27	0 10 0	58	- 60	2	145	-135	8	29	- 23	4	10	- 8
4	156	162	1	98	89	3	75	- 86	1 5 2	136	114	5	77	- 90
5	157	165	2	67	57	4	91	95	2	95	108	6	10	6
6	5	- 5	0 0 1	201	199	5	62	58	3	64	- 71	7	125	-122
7	94	-113	2	181	-156	6	35	30	4	119	-143	8	5	6
8	49	48	4	130	-109	7	69	68	5	39	42	0 4 3	34	- 45
9	55	- 58	6	186	214	0 8 1	85	- 91	6	20	- 21	1	173	155
1 3 0	191	-221	8	28	- 28	1	131	-140	7	88	84	2	80	76
2	43	- 39	1 1 1	46	36	2	22	17	8	124	126	3	49	42
3	173	178	2	226	-265	3	51	- 47	0 6 2	161	126	4	42	47
4	28	33	3	138	-115	4	40	47	1	10	7	5	127	-124
5	66	- 71	4	129	112	5	126	109	2	129	-113	6	93	- 93
6	23	16	5	59	64	6	51	- 40	3	10	- 16	7	63	64
7	113	-121	6	53	52	1 9 1	73	- 64	4	157	-144	8	20	19
8	18	- 25	7	63	75	2	35	- 42	5	21	- 23	1 5 3	43	45
9	86	90	8	105	- 95	3	162	131	6	76	70	2	156	186
0 4 0	79	-118	9	53	- 68	4	15	- 8	7	13	15	3	68	- 80
1	204	203	0 2 1	128	-121	5	49	- 46	1 7 2	115	123	4	73	- 83
2	109	115	1	277	-244	0 10 1	65	- 55	2	126	-129	5	21	12
3	28	31	2	66	51	1	96	83	3	66	- 76	6	45	- 43
4	135	174	3	113	- 90	2	48	41	4	130	91	7	37	36
5	163	-179	4	51	49	3	0	6	5	32	22	0 6 3	159	156
6	19	- 11	5	171	155	0 0 2	240	245	6	24	34	1	32	29
7	87	86	6	95	- 97	2	203	-183	0 8 2	111	- 84	2	60	- 69
8	46	48	7	54	- 65	4	261	-242	1	124	-109	3	32	29
9	51	60	8	19	8	6	105	98	2	5	- 4	4	62	- 69
1 5 0	10	- 6	9	25	- 19	8	69	- 69	3	5	8	5	5	- 7
2	96	92	1 3 1	83	- 80	1 1 2	162	150	4	17	- 17	6	171	155
3	116	-132	2	23	- 32	2	250	-195	5	139	125	1 7 3	10	15
4	132	-157	3	215	215	3	58	- 56	6	94	-102	2	155	-120
5	10	12	4	20	- 10	4	188	170	1 9 2	64	- 61	3	91	- 81
6	22	- 10	5	98	-100	5	37	33	2	38	36	4	90	86
7	29	30	6	10	7	6	45	48	3	161	155	5	48	49
8	137	136	7	134	-131	7	61	63	4	25	27	6	29	28
0 6 0	277	296	8	10	7	8	163	-140	0 10 2	151	-142	0 8 3	82	- 66
1	21	- 16	9	115	127	9	14	- 19	1	88	- 74	1	131	-125
2	5	3	0 4 1	86	- 76	0 2 2	172	-177	2	11	- 14	2	33	28
3	39	- 41	1	212	184	1	143	-101	0 0 3	183	188	3	45	- 42
4	71	- 76	2	73	65	2	60	- 43	2	90	- 97	4	55	53
5	22	- 15	3	52	51	3	61	62	4	76	- 73	5	89	99
6	132	146	4	37	31	4	35	- 25	6	184	204	1 9 3	57	- 62
7	28	33	5	133	-140	5	145	142	8	15	- 14	2	37	- 37
8	9	12	6	99	-120	6	111	-116	1 1 3	29	27	3	110	116
1 7 0	72	75	7	70	70	7	149	-127	2	180	-214	9 10 3	30	- 40
2	115	-101	8	16	9	8	17	- 14	3	103	-103			
3	145	-153	1 5 1	57	58	9	49	- 53	4	95	98			

Table 4. *Observed and calculated structure factors of* $Bi_2Al_4O_9$

h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c
2 0 0	100	-121	3 7 0	145	-135	9 4 1	10	- 16	8 2 2	45	46	4 1 3	173	169
4	122	-147	4	123	117	1 5 1	39	42	9	41	42	5	53	44
6	199	251	5	17	20	2	173	175	1 3 2	146	-115	6	0	- 12
8	45	- 55	6	20	- 28	3	109	- 96	2	0	- 8	7	0	13
1 1 0	0	11	7	36	33	4	173	-159	3	291	296	8	96	-104
2	111	-145	0 8 0	84	- 88	5	62	48	4	0	9	0 2 3	116	-104
3	102	-128	1	100	-104	6	0	9	5	74	- 71	1	179	-189
4	145	175	2	80	69	7	23	20	6	0	3	2	79	50
5	49	55	3	25	17	8	94	99	7	64	- 57	3	0	6
6	52	- 45	4	72	73	0 6 1	159	162	8	0	- 8	4	30	31
7	0	7	5	76	81	1	0	1	9	118	142	5	156	143
8	90	- 93	6	50	- 55	2	112	- 98	0 4 2	115	-165	6	87	- 74
9	75	- 87	1 9 0	96	- 90	3	0	1	1	180	150	7	124	-126
0 2 0	124	-117	2	0	3	4	72	- 60	2	48	41	8	53	44
1	145	-173	3	128	134	5	10	- 2	3	28	- 24	1 3 3	117	- 94
2	110	118	4	11	- 8	6	138	127	4	52	41	2	0	- 3
3	23	19	0 10 0	49	- 51	7	0	1	5	113	-112	3	193	161
4	105	103	1	104	84	1 7 1	22	30	6	114	-107	4	0	2
5	104	108	2	56	55	2	146	-137	7	118	123	5	137	-108
6	67	- 62	0 0 1	238	238	3	81	- 71	8	17	25	6	0	1
7	116	-121	2	147	-150	4	152	131	1 5 2	109	113	7	47	- 41
8	64	65	4	77	- 80	5	46	41	2	107	102	8	0	- 2
9	41	39	6	127	161	6	0	- 13	3	114	- 96	0 4 3	87	- 88
1 3 0	138	-151	8	96	-107	7	12	13	4	129	-120	1	170	168
2	61	- 58	1 1 1	40	45	0 8 1	82	- 79	5	77	60	2	59	45
3	216	228	2	181	-228	1	127	-136	6	45	35	3	0	- 7
4	0	6	3	99	-114	2	46	37	7	72	62	4	23	26
5	151	-153	4	159	197	3	0	4	8	53	66	5	142	-130
6	21	24	5	49	54	4	35	23	0 6 2	136	167	6	82	- 67
7	89	- 88	6	0	- 13	5	101	109	1	0	13	7	131	119
8	0	- 5	7	0	17	6	62	- 64	2	122	-120	8	44	41
9	112	134	8	103	-115	1 9 1	64	- 63	3	0	13	1 5 3	31	33
0 4 0	100	- 92	9	53	- 62	2	0	- 2	4	108	- 83	2	171	153
1	195	208	0 2 1	141	-137	3	115	120	5	0	- 9	3	122	- 88
2	100	109	1	198	-233	4	0	1	6	121	136	4	154	-141
3	0	15	2	57	52	0 10 1	53	- 55	7	0	- 11	5	54	40
4	105	84	3	0	7	1	97	105	1 7 2	78	73	6	0	9
5	159	-140	4	26	29	2	28	27	2	112	-115	7	17	16
6	78	- 73	5	161	163	0 0 2	281	279	3	67	- 73	0 6 3	148	149
7	109	108	6	91	- 87	2	172	-182	4	122	110	1	0	1
8	63	65	7	134	-141	4	124	-133	5	69	67	2	94	- 84
9	21	- 16	8	47	45	6	144	194	6	12	- 15	3	0	- 0
1 5 0	27	26	1 3 1	118	-108	8	83	-110	0 8 2	98	- 99	4	65	- 51
2	114	108	2	0	- 3	1 1 2	88	105	1	104	-111	5	0	- 1
3	143	-128	3	211	188	2	181	-206	2	24	31	6	126	119
4	148	-126	4	0	3	3	68	- 71	3	0	5	1 7 3	21	25
5	60	46	5	153	-118	4	152	154	4	20	20	2	150	-122
6	48	37	6	0	1	5	79	92	5	73	85	3	78	- 68
7	12	18	7	50	- 42	6	0	- 8	1 9 2	48	- 49	4	132	118
8	60	68	8	0	- 2	7	49	- 50	2	26	23	5	36	35
0 6 0	212	241	9	100	116	8	75	- 83	3	136	152	0 8 3	79	- 69
1	15	- 12	0 4 1	108	-110	9	45	- 49	4	5	- 5	1	115	-122
2	79	- 77	1	175	196	0 2 2	139	-107	0 0 3	225	198	2	42	36
3	0	- 11	2	49	45	1	145	-124	2	137	-114	3	0	4
4	63	- 53	3	0	- 8	2	39	43	4	68	- 66	4	33	24
5	0	6	4	21	24	3	57	45	6	127	148	1 9 3	61	- 60
6	183	176	5	170	-146	4	0	- 9	8	93	- 94			
7	0	6	6	90	- 76	5	80	88	1 1 3	26	34			
1 7 0	52	54	7	138	131	6	105	-110	2	194	-185			
2	103	-104	8	50	42	7	111	-128	3	119	-100			

and 0.10 for $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$, and $Bi_2Fe_4O_9$ respectively. The comparison between the observed and computed structure factors are listed in Tables 3, 4 and 5.

Discussion of the structures

The interatomic distances between the neighboring atoms are tabulated in Table 6, which is classified according to the kind of the metal-oxygen coordination polyhedron. These polyhedra are graphically shown in Fig. 2. The distances are also shown in the schematic representation of the structures, Figs. 3, 4 and 5. In Figs. 6 and 7, the three-dimensional structural schemes of $Bi_2Mn_4O_{10}$ and $Bi_2Al_4O_9$ are respectively illustrated.

A significant difference between the two structures illustrated in Figs. 6 and 7 is found only in the coordination of oxygen atoms

Table 5. *Observed and calculated structure factors of* $Bi_2Fe_4O_9$

h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c
2 0 0	107	-109	9 5 0	74	- 86	2 2 1	74	60	7 7 1	8	- 9	0 4 2	181	-190
4	107	-112	0 6 0	271	273	3	17	15	0 8 1	98	- 90	1	138	132
6	270	272	1	51	- 52	4	-	1	1	103	-113	2	8	10
8	59	- 44	2	83	- 63	5	177	152	2	55	50	3	59	- 50
1 1 0	40	- 32	3	8	- 8	6	98	- 77	3	8	8	4	17	16
2	123	-105	4	21	- 21	7	118	-132	4	8	11	5	80	- 69
3	175	-174	5	34	34	8	63	61	5	77	78	6	107	-103
4	172	162	6	169	173	9	33	30	6	77	- 64	7	139	116
5	34	34	7	17	- 17	1 3 1	82	- 76	1 9 1	40	- 39	8	0	2
6	98	- 88	8	50	- 57	2	17	18	2	34	28	9	70	- 60
7	25	- 27	1 7 0	17	17	3	154	150	3	78	83	1 5 2	169	158
8	42	- 42	2	90	- 69	4	17	- 18	4	34	- 31	2	53	64
9	80	- 81	3	102	-116	5	137	-136	5	60	- 72	3	132	-112
0 2 0	136	-121	4	109	109	6	4	6	0 10 1	0	- 10	4	107	- 97
1	135	-135	5	13	- 11	7	17	14	1	91	110	5	121	95
2	199	187	6	65	- 65	8	8	6	2	4	5	6	74	57
3	59	55	7	8	10	9	78	77	3	13	- 12	7	78	71
4	134	140	0 8 0	93	- 98	0 4 1	68	- 65	0 0 2	287	278	8	21	23
5	55	55	1	68	- 71	1	245	231	2	219	-238	0 6 2	126	147
6	55	- 55	2	96	103	2	30	30	4	148	-155	1	25	- 20
7	108	-111	3	25	24	3	22	- 19	6	169	160	2	142	-145
8	90	85	4	78	83	4	8	- 7	8	143	-128	3	17	15
9	76	70	5	34	38	5	148	-145	1 1 2	118	148	4	84	- 84
1 3 0	214	-196	6	62	- 56	6	51	- 45	2	171	-173	5	13	11
2	42	- 44	1 9 0	93	-101	7	130	133	3	46	- 45	6	108	103
3	216	203	2	34	31	8	38	38	4	149	153	7	38	- 28
4	13	- 9	3	118	115	9	42	- 32	5	106	120	8	87	-104
5	187	-190	4	38	- 35	1 5 1	49	37	6	54	- 46	1 7 2	71	72
6	29	33	5	84	- 90	2	186	165	7	51	54	2	103	- 85
7	79	- 71	0 10 0	13	12	3	126	- 99	8	42	- 44	3	21	- 20
8	4	- 3	1	67	73	4	139	-149	9	25	- 22	4	126	104
9	75	91	2	38	41	5	76	71	0 2 2	193	-184	5	61	60
0 4 0	44	- 57	3	33	- 27	6	17	20	1	86	- 87	6	59	- 49
1	202	193	4	17	24	7	4	- 5	2	34	26	7	42	41
2	114	134	0 0 1	186	190	8	59	67	3	94	74	0 8 2	152	-135
3	21	- 20	2	153	-154	0 6 1	110	124	4	0	- 3	1	81	- 78
4	115	105	4	25	- 23	1	37	- 32	5	29	33	2	42	33
5	105	-103	6	138	123	2	104	- 95	6	141	-130	3	17	13
6	34	- 33	8	107	-126	3	8	6	7	116	-113	4	4	4
7	100	108	1 1 1	25	24	4	17	- 18	8	51	42	5	49	46
8	54	63	2	236	-255	5	17	19	9	97	76	6	106	- 97
9	58	- 49	3	72	- 87	6	97	90	1 3 2	99	- 85	1 9 2	34	- 35
1 5 0	25	22	4	245	218	7	28	- 23	2	4	6	2	51	50
2	79	67	5	61	62	8	82	- 93	3	306	334	3	135	154
3	193	-188	6	37	- 30	1 7 1	0	5	4	13	- 11	4	38	- 35
4	98	-103	7	13	- 13	2	142	-151	5	80	- 63	0 10 2	44	- 56
5	55	44	8	90	- 90	3	25	- 27	6	10	10	1	80	69
6	55	61	9	42	- 40	4	135	144	7	15	- 18	2	10	- 7
7	4	- 4	0 2 1	145	-128	5	25	25	8	0	- 2			
8	25	24	1	253	-257	6	25	- 26	9	125	134			

Table 6. *Bond lengths and bond angels in* $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$ *and* $Bi_2Fe_4O_9$

(i) Octahedral M—O coordinations

	$Bi_2Mn_4O_{10}$	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$	notation (Fig. 7*a*)
M—O(2)	1.83 Å	1.84 Å	1.95 Å	*a*
M—O(3)	1.90	1.93	1.95	*b*
M—O(4)	1.98	1.87	2.05	*c*
O(2)—O(3)	2.64	2.69	2.82	*d*
O(2)—O(3′)	2.57	2.60	2.79	*e*
O(2)—O(4)	2.59	2.69	2.80	*f*
O(2)—O(4′)	2.59	2.66	2.76	*g*
O(3)—O(3′)	2.62	2.42	2.58	*h*
O(3)—O(4)	2.88	2.86	3.01	*j*
O(4)—O(4′)	2.56	2.51	2.69	*k*
O(3)—M—O(4)	96.1°	98.4°	97.4°	α
O(4)—M—O(4′)	80.5	84.2	82.1	β
O(2)—M—O(3)	93.4	92.6	92.7	γ
O(2)—M—O(4)	88.4	91.3	91.0	δ
O(2)—M—O(3′)	89.9	90.0	88.8	ε
O(2)—M—O(4′)	88.1	91.9	87.4	ξ

Table 6. *(Continued)*

(ii) Square-pyramidal Mn—O coordination

	$Bi_2Mn_4O_{10}$	notation (Fig. 7*b*)		
Mn—O(1)	1.91 Å	*a*	O(1)—Mn—O(1′)	82.9°
Mn—O(2)	2.10	*b*	O(2)—Mn—O(2′)	86.7
Mn—O(3)	2.04	*c*	O(3)—Mn—O(1)	97.0
			O(3)—Mn—O(2)	100.4
O(3)—O(1)	3.03	*d*	O(1)—Mn—O(2)	92.6
O(3)—O(2)	3.10	*e*		
O(1)—O(2)	2.90	*f*		
O(1)—O(1′)	2.53	*g*		
O(2)—O(2′)	2.88	*h*		

(iii) Tetrahedral Al—O and Fe—O coordinations

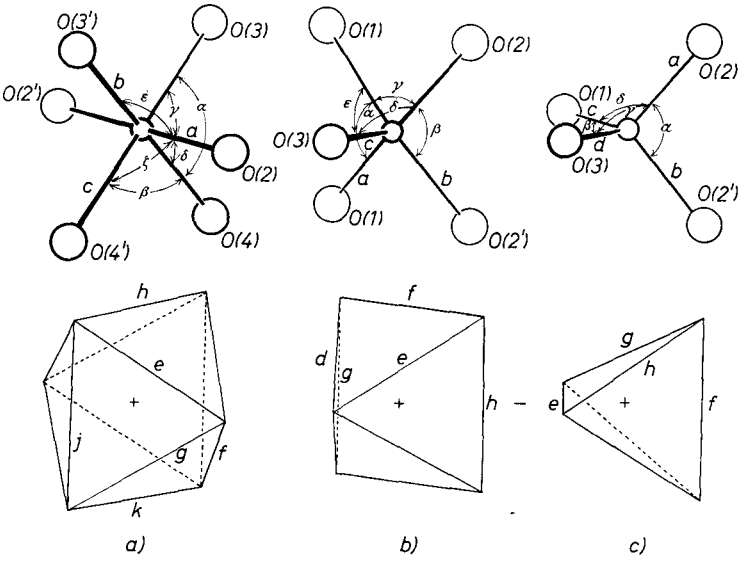
	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$	Notation (Fig. 7*c*)
M—O(2)	1.83 Å	1.93 Å	*a*
M—O(2′)	1.83	1.93	*b*
M—O(1)	1.76	1.83	*c*
M—O(3)	1.77	1.84	*d*
O(1)—O(3)	2.83	2.97	*e*
O(2)—O(2′)	2.85	3.08	*f*
O(3)—O(2)	2.96	3.14	*g*
O(1)—O(2)	3.00	3.06	*h*
O(2)—M—O(2′)	102.3°	106.1°	α
O(3)—M—O(1)	106.6	107.6	β
O(2)—M—O(3)	113.0	108.2	γ
O(2)—M—O(1)	111.1	113.3	δ

(iv) Bi—O coordination (three shortest bonds)

	$Bi_2Mn_4O_{10}$	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$	Notation (Fig. 7*d*)
Bi—O(2)	2.07 Å	2.11 Å	2.23 Å	*a*
Bi—O(4)	2.15 (2×)	2.18 (2×)	2.23 (2×)	*b*
O(2)—Bi—O(4)	85.3°	82.1°	86.7°	α
O(4)—Bi—O(4′)	89.2	86.7	89.3	β

around M(2) ions, which is indicated in the figures by black coloring of spheres. In $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$ structures (Fig. 7) the coordination is tetrahedral, while in $Bi_2Mn_4O_{10}$ structure (Fig. 6) it is square pyramidal. The position of Mn(2) ion is slightly (about 0.03 Å) shifted toward the apex of pyramid from the center of the square base. Since three oxygen atoms surrounding M(2) ion, i.e. O(3) and two O(2)'s are located in approximately identical geometry in both structures, the difference is due to whether another oxygen atom, O(1), is at equipoint $2b$ or at $4e$. The bond lengths and bond angles found in these coordination polyhedra are tabulated in groups (ii) and (iii) of Table 6. If the sixth neighboring oxygen atom is sought, it is located at 2.94 Å from the Mn(2). This weak bond is indicated by dotted line in Fig. 2.

Manganese in the various oxide structures, MnO, Mn_2O_3, and MnO_2 is known to have octahedral coordination, although in Mn_3O_4, which



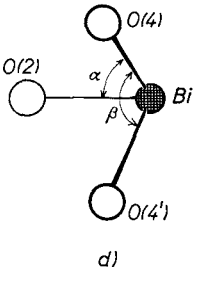


Fig. 2. Coordination polyhedra and bond systems found in the structures of $Bi_2Mn_4O_{10}$, $Bi_2Al_4O_9$, and $Bi_2Fe_4O_9$; (*a*) octahedral, (*b*) square-pyramidal, (*c*) tetrahedral, and (*d*) Bi–O coordinations. Roman letters accompanying the straight lines indicate the kind of bond, and their lengths are listed in Table 6. Greek letters indicate the bond angles, and their values are also listed in Table 6. Large circles represent oxygen, small circles metal, and cross-hatched circles bismuth atoms

has a distorted spinel structure, one kind of Mn is coordinated by four oxygen atoms arranged in the shape of square instead of tetrahedral arrangement in regular spinel. Nature of the square bond was discussed by SINHA and SINHA[6] as the result of hybrid orbitals. The square-pyramidal coordination found in the present study was also reported in $HoMn_2O_5$[4], the structure of which is same as $BiMn_2O_5$ except the difference found in the coordination around Ho and Bi ions as discussed below. The coordination of oxygen atoms in the

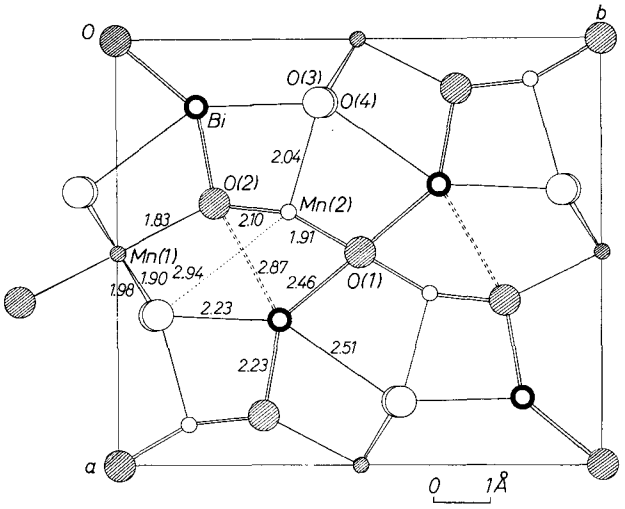


Fig. 3. Schematic representation of the structure of $Bi_2Mn_4O_{10}$. The structure is represented in the full unit cell of the projection on (001). The open circles indicate the atoms at $z = 0$ or $1/2$, and the shaded circles those at nearly $1/4$ or $3/4$. The chemical bonds between the neighboring atoms are shown by straight lines for the nearest, by dashed lines for the second- and the third-nearest neighbors. Dotted line is used to indicate the weaker Mn—O bond. The figures accompanying these bonds are interatomic distances in Å

same square-pyramidal shape around the central V ion is reported in a few structures, V_2O_5[7], $K_3V_5O_{14}$[8] and $SrVSi_2O_7$ (mineral haradaite)[9].

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[6] K. P. SINHA and A. P. B. SINHA, Valency distribution and bonding in some oxides of spinel structure. J. Physic. Chem. **61** (1957) 758—761.

[7] H. G. BACHMANN, F. R. AHMED and W. H. BARNES, The crystal structure of vanadium pentoxide. Z. Kristallogr. **115** (1961) 110—113.

[8] A. M. BYSTROM and T. E. EVANS, The crystal structure of $K_3V_5O_{14}$. Acta Chim. Scand. **13** (1959) 377—378.

[9] Y. TAKÉUCHI and W. JOSWIG, The structure of haradaite and a note on the Si—O bond length in silicates. Mineral. Journal **5** (1967) 98—123.

The coordination polyhedra of Mn(1)-O as well as of Fe(1)-O and Al(1)-O are all octahedra, bond lengths and bond angles of which are tabulated as group (i) of Table 6.

The bond lengths and bond angles associated with Bi—O coordination are tabulated in group (iv) of Table 6 for the shortest three

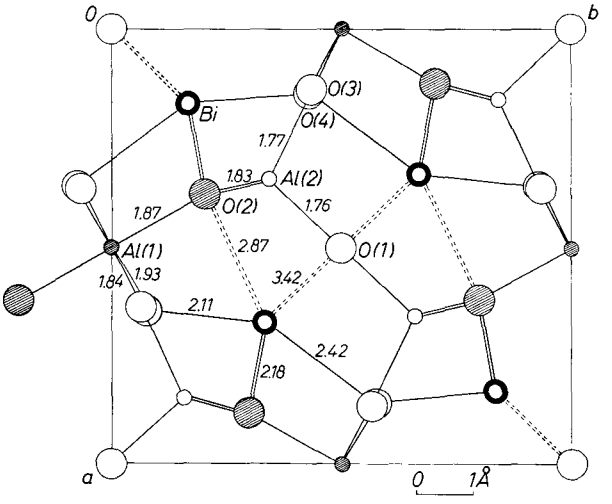

Fig. 4. Schematic representation of the structure of $Bi_2Al_4O_9$. Explanations for symbols and figures are same as in Fig. 2

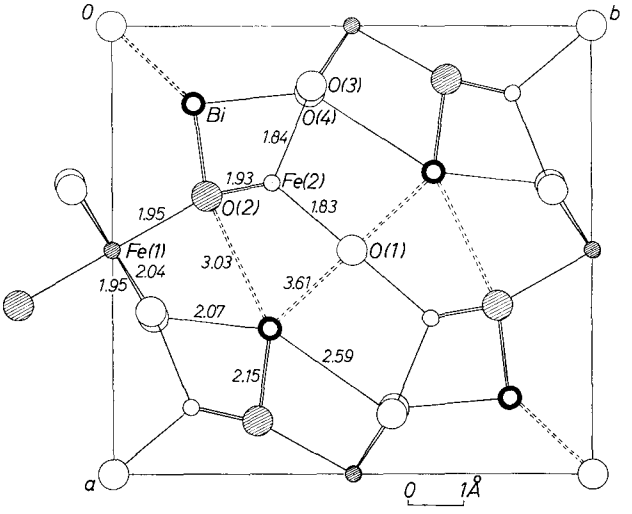

Fig. 5. Schematic representation of the structure of $Bi_2Fe_4O_9$. Explanations for symbols and figures are same as in Fig. 2

bonds. The longer interatomic distances are indicated in Figs. 3, 4 and 5. The Bi—O bonds in the three structures presently discussed are all distinctly directional. This is in contrast to the Ho—O bonds in

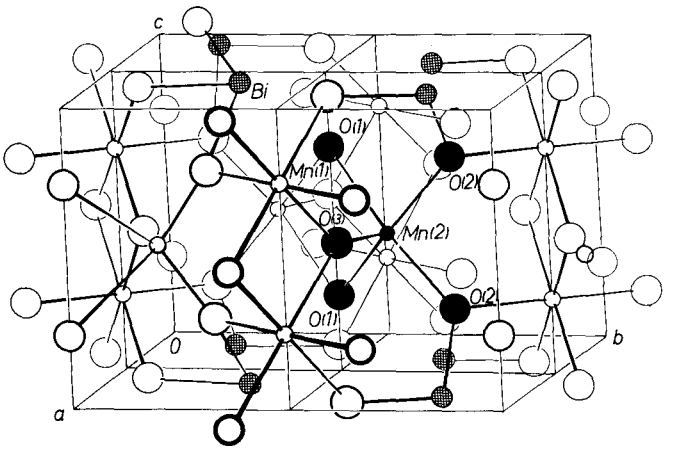

Fig. 6. Structural sheme of $Bi_2Mn_4O_{10}$. Large circles represent oxygen, small circles managnese, and cross-hatched circles bismuth atoms. A square-pyramidal coordination is indicated by black coloring of related atoms

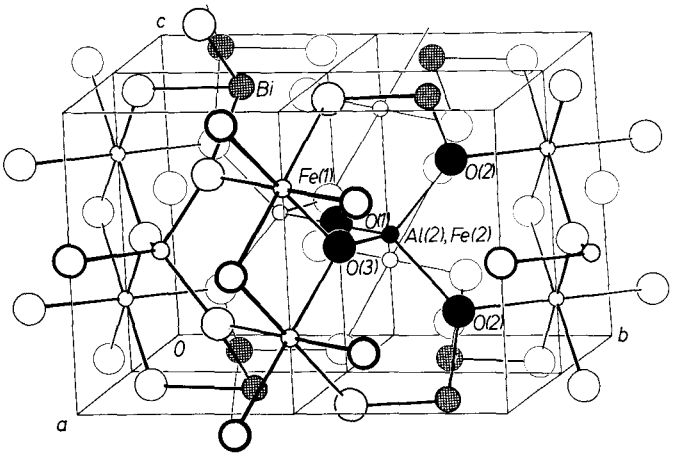

Fig. 7. Structural scheme of $Bi_2Al_4O_9$, and $Bi_2Fe_4O_9$. Large circles represent oxygen, small circles aluminum or iron, and cross-hatched circles bismuth atoms. A tetrahedral coordination is indicated by black coloring of related atoms

$HoMn_2O_5$[4], in which Ho is located at the center of a trigonal prism formed by six oxygen atoms. The three shortest bonds shown in Fig. 2*d* are nearly orthogonal to each other. If the second- and third-

nearest neighbors are considered Bi ions are surrounded by eight oxygen atoms.

In building up the three-dimensional structures illustrated in Figs. 6 and 7, the isolated BiO_3 groups are connected along c axes sharing oxygen atoms with M(2) ions. Along a and b axes, M(1) ions play the role of connecting together these groups. The nature of coordination in Bi-O in the present double oxides is similar to the Bi-S coordination in sulfosalts structures. If the $Bi_2Al_4O_9$-type structure is expressed in terms of the coordination polyhedra, the following formula is obtained: $Bi_2M_2^{\text{tetrahedral}}M_2^{\text{octahedral}}O_9$. Although the corresponding sulfosalts is not known to occur in nature, it may be worth-while to synthesize and to study the structure of such a compound as $CuFeBiS_3$, which satisfies the above condition for the coordination.

Acknowledgement

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